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INVESTOR IN PEOPLE #2

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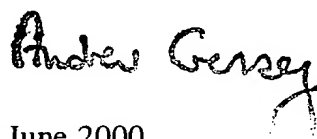
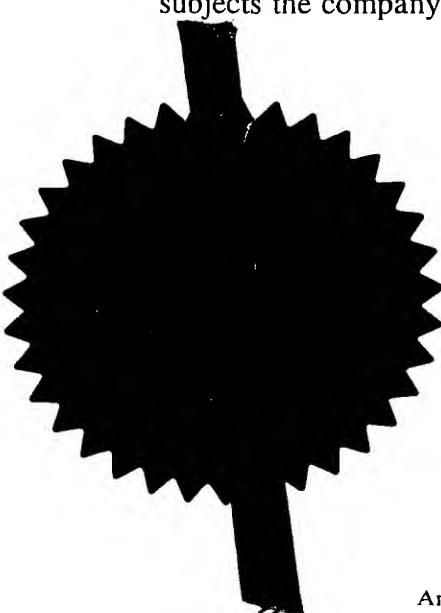
I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

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Dated 20 June 2000

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# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference IPD/P2355

2. Patent application number  
(The Patent Office will fill in this part)

9914041.0

17 JUN 1999

3. Full name, address and postcode of the or of each applicant (underline all surnames)

THE SECRETARY OF STATE FOR DEFENCE  
Defence Evaluation and Research Agency  
Ively Road, Farnborough  
Hampshire GU14 0LX, UK

Patents ADP number (if you know it)

7349996001

If the applicant is a corporate body, give the country/state of its incorporation

GB

IS

4. Title of the invention

Novel Process

5. Name of your agent (if you have one)

Sedgwick, Freda

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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A O Bowdery

D/IPR Fmls Sec (DERA)

Poptar 2

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BRISTOL U BS34 8JH

7665003001

6935910003

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number or earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77

I

# Novel Process

The present invention relates to processes for the production of sulphides, in particular lithiated transition metal sulphides useful in the production of batteries, and to the use of molten sulphur as a solvent in such processes.

In the 1980's, there was extensive research into lithium-metal rechargeable batteries, particularly using sulphides (and selenides) as the cathode materials. Many lithium metal/molybdenum disulphide ( $\text{Li}/\text{MoS}_2$ ) batteries were produced but these had to be withdrawn following a fire. Other sulphides (iron disulphide  $\text{FeS}_2$ , titanium disulphide  $\text{TiS}_2$ ) and niobium triselenide  $\text{NbSe}_3$  were particularly investigated as alternative cathode materials.

Although the use of lithium metal rechargeable batteries is now limited (due to fears of further battery fires), they are used in the laboratory testing of materials. Lithium metal primary batteries using iron disulphide cathodes are manufactured.

Virtually all modern lithium rechargeable batteries are of the lithium-ion type, in which the lithium is absorbed in carbon, in the negative electrode (anode). These use a lithiated cathode, which is usually lithium cobalt oxide  $\text{LiCoO}_2$ , although lithium nickel oxide  $\text{LiNiO}_2$ , lithium manganese oxide  $\text{LiMn}_2\text{O}_4$ , and mixed oxides are also known.

The main applications of lithium rechargeable batteries at present are limited to premium applications, such as portable computers or telephones, because their high cost is prohibitive for other applications. To get into wider markets, such as electric vehicles, the cost must be reduced. Hence there is a strong demand for high performance (i.e. lithium-ion) batteries at much more economical prices.

The applicants have developed an economical synthesis which can be operated on a large scale to produce sulphides, or mixtures of sulphides, which have useful electrochemical properties.

- 5 The present invention provides a process for the production of a lithiated transition metal sulphide, said process comprising reacting a transition metal sulphide with lithium sulphide in a solvent comprising molten sulphur.
- 10 Suitably the transition metal sulphide used in the process is an iron, molybdenum, niobium or titanium sulphide and is preferably iron. Ferrous sulphide is, as mentioned above, an inexpensive and readily available mineral product.
- 15 The reaction is carried out at elevated temperature, which is sufficient to melt the sulphur to allow it to act as solvent, i.e. between 95.5°C and 444°C. However, the reaction proceeds more rapidly than previously known processes. On a laboratory scale, the reaction can be completed in a few hours, and this
- 20 depends largely on the heating time of the furnace.

Lithium sulphide may be bought commercially. It would be more economical however on a large scale to produce the lithium sulphide by reduction of lithium sulphate, for example by using

25 a conventional method in which lithium sulphate is heated with carbon to the melting point of lithium sulphate (860°C).

The sulphur used as the solvent is inexpensive, but it is preferably recovered for example by dissolving it out of the

30 product using solvent extraction by shaking the product with a solvent such as carbon disulphide. Alternatively, sulphur can be removed by vapourisation, for example by heating the product/sulphur mixture above the boiling point of sulphur (440°C) for example at about 500°C. It may then be recycled to

5

and held at this temperature for about an hour. The temperature was then increased to 500°C to vapourise surplus sulphur. After cooling, the product was removed from the furnace and stored in an inert atmosphere glove box, to avoid  
5 reaction with moisture in air.

The product was analysed by X-ray diffraction analysis which showed that the main components were lithiated iron sulphide of various compositions,  $\text{Li}_2\text{Fe}_2\text{S}_4$ ,  $\text{Li}_2\text{Fe}_2\text{S}_6$  and  $\text{Li}_2\text{FeS}_2$ , with a small  
10 amount of iron disulphide (pyrites),  $\text{FeS}_2$ , as an impurity. This material was then tested for use in a laboratory cells as described previously in A. Gilmour, C.O. Giwa, J.C. Lee and A.G. Ritchie, Lithium Rechargeable Envelope Cells, Journal of Power Sources, volume 65, pp219-224 (1997), Power Sources 16.  
15 The lithiated iron sulphide was made into a battery cathode by coating a slurry of it with a binder, ethylene propylene diene monomer (EPDM) dissolved in cyclohexane together with a conductive additive of carbon, using a doctor blade coating technique.

20

The cathode was electrically cycled against an anode of graphite using an electrolyte of ethylene carbonate/diethylcarbonate/ lithium hexafluorophosphate,  $\text{LiPF}_6$ . Charge/discharge (cycling) curves are illustrated in Figure 1.  
25 This shows that the product could be charged and discharged using standard conditions.

11. A lithiated transition metal sulphide obtainable by a process according to any one of the preceding claims.
12. An electrode containing a lithiated transition metal sulphide according to claim 11 as the cathode.
13. A battery comprising an electrode according to claim 12.
14. A battery according to claim 13 wherein said electrode is a cathode and the anode comprises a lithium ion anode.
15. A battery according to claim 13 or claim 14 which is a rechargeable battery.
16. The use of sulphur in a molten state as a solvent in a chemical reaction.
17. The use according to claim 16 wherein the chemical reaction is the production of a sulphide.
18. The use according to claim 17 wherein the sulphide is a lithiated transition metal sulphide.
19. A method for producing a lithiated transition metal sulphide substantially as hereinbefore described with reference to the Example.

# Li-ion $\text{Li}_x\text{Fe}_y\text{S}_z$ cell cycling

(0.5mA/cm<sup>2</sup>)

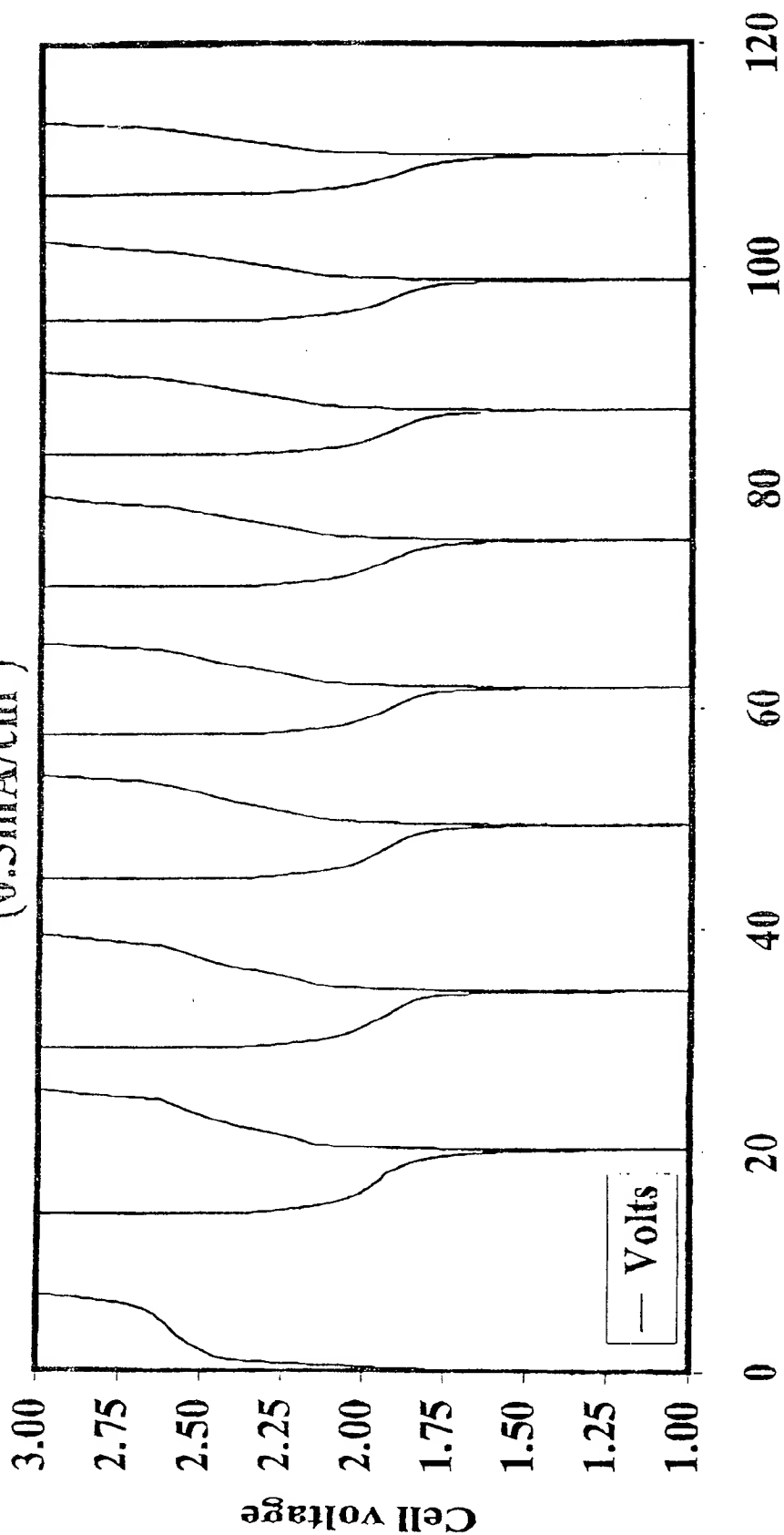


Figure 1